



Making the Best

Environmentalists have high hopes for hydrogen as a fuel. Hydrogen burns cleanly, with water its only combustion by-product—a marked contrast to traditional fossil fuels, which produce all manner of pollutants, including carcinogenic toxicants and greenhouse gases.

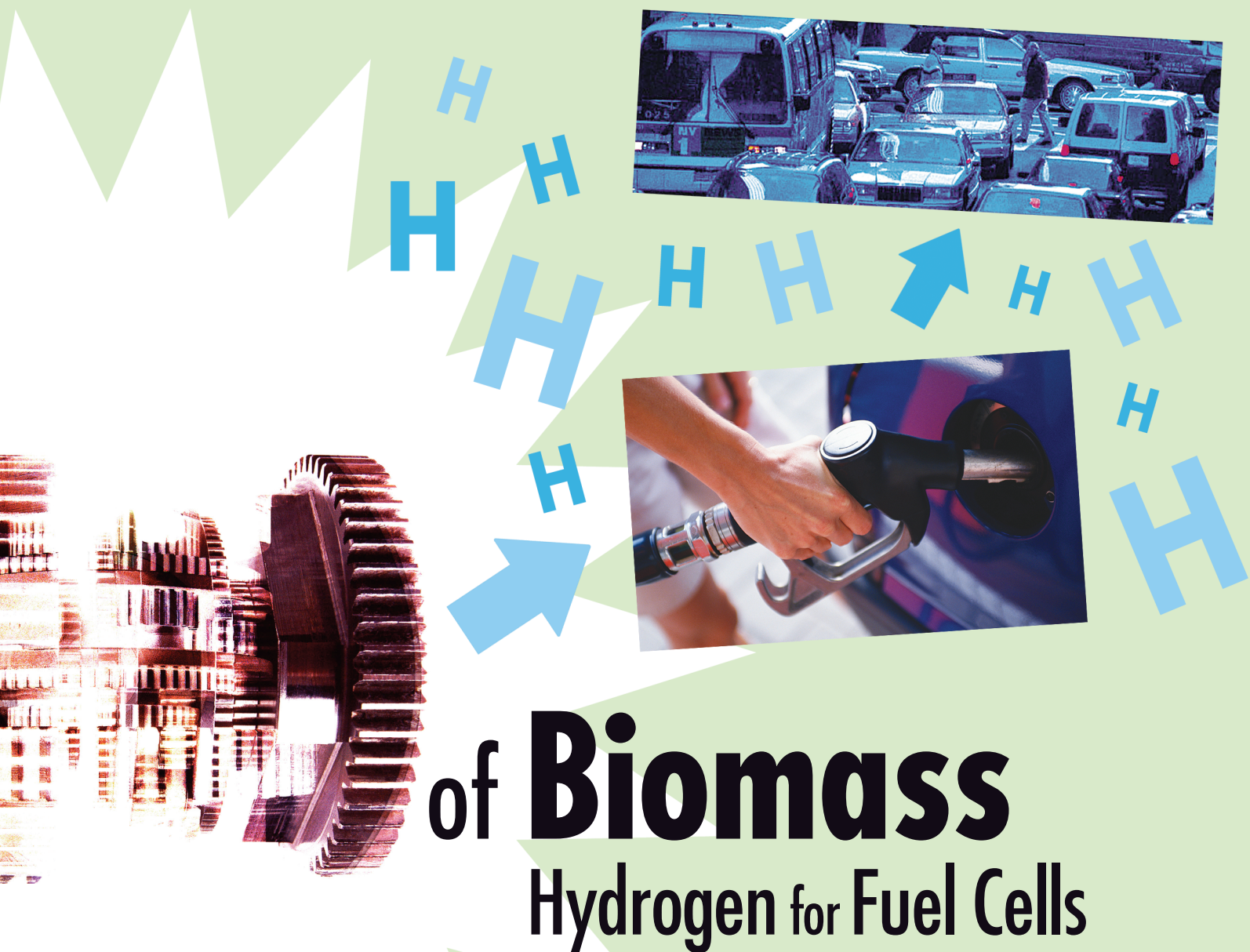
But there's a catch: virtually all current processes for producing hydrogen themselves release greenhouse gases. Now scientists are working on several promising (although not yet commercially viable) techniques that may someday solve the puzzle of providing inexpensive, mobile, cleaner sources of hydrogen.

Hydrogen: The Fuel of the Future?

Despite the element's promise as a fuel, a dearth of economical and Earth-friendly ways to produce pure

hydrogen is slowing adoption of hydrogen-powered technologies. The problem isn't a lack of hydrogen; it's the most abundant element on the Earth's surface. But naturally occurring hydrogen is invariably locked up in molecules, as in water, hydrocarbons, or plants. To use hydrogen for fuel, it must be liberated from other elements.

Most commercially produced hydrogen is used for manufacturing ammonia and methanol and for hydrogenating fats and oils (this makes liquid oils semisolid, makes them less likely to become rancid, and improves the appearance of fats). Small quantities are also used in such applications as welding and the production of rocket fuel and hydrochloric acid. Currently virtually all commercially produced hydrogen is extracted by applying heat and steam to hydrocarbons in fossil fuels, most



of Biomass

Hydrogen for Fuel Cells

often natural gas but sometimes gasoline or coal. This process, called “steam reforming,” also releases carbon dioxide (CO_2), a greenhouse gas.

Proponents of hydrogen as a fuel, however, say that the element’s future lies in electricity-generating fuel cells. A fuel cell is much like a battery in that it consists of an anode connected to a cathode by an electrolyte. But unlike a battery’s captive chemical source of electrons, which over time becomes depleted, a fuel cell needs an external, ongoing source of electrons, such as hydrogen. Hydrogen fuel cells have already started to appear in industrial settings, where they augment conventional power sources. Fuel cells also provide backup for businesses, such as hospitals and financial operations, where an uninterrupted supply of electricity is critical.

As fuel cell technology advances, the devices are expected to crop up in remarkably diverse settings. They are the critical component of the Department of Energy’s (DOE) FreedomCar program, a joint effort between the government and industry to develop fuel cell-powered automobiles and new ways of producing hydrogen. Although FreedomCar is a recent initiative, fuel cells already appear in cars by such companies as Toyota, Mercedes-Benz, and Honda. In November 2002, energy secretary Spencer Abraham announced a “roadmap” for bringing widespread use of fuel cells to the nation’s cars and trucks. This, he said, further committed the United States to a hydrogen-based transportation system. The roadmap describes routes to production, delivery, storage, conversion to useful power, and applications for hydrogen fuel.

Public transportation may pave the way for adoption of fuel cell vehicles. In 2003, 10 European cities—Amsterdam, Barcelona, Hamburg, London, Luxembourg, Madrid, Porto, Reykjavík, Stockholm, and Stuttgart—are scheduled to begin using 30 Mercedes-Benz Citaro fuel cell-powered buses. About a year later, the Santa Clara Valley Transportation Authority in San Jose, California, will introduce fuel cell-powered buses as part of a two-year experiment during which such factors as safety, ease of maintenance and operation, and public acceptance will be evaluated.

Fuel cells are also being developed for other applications in which it is not only desirable but necessary to keep combustion by-product emissions to a minimum. For example, a prototypical fuel cell-powered locomotive for underground mining has been tested in Québec, Canada, in a joint U.S. DOE and Canadian project. Another promising application is the provision of electricity to remote locations, from American farms to villages in developing nations. Just as mobile telephones have brought communications to villages far removed from any phone-line infrastructure, fuel cells can bring electricity to locations without the expense of constructing power lines, says Daniel Kammen, a professor in the Energy and Resources Group and director of the Renewable and Appropriate Energy Laboratory at the University of California at Berkeley.

But improving fuel cells isn't enough to make these applications practical, Kammen says. An infrastructure to distribute hydrogen is also essential. Kammen says there's a proposal in California for a "hydrogen corridor" between Sacramento and San Francisco that will include hydrogen fueling stations, other stations where cars can be plugged in to actually add electricity to the power grid, and photovoltaic hydrogen production (to generate hydrogen in remote locations where a pipeline wouldn't be possible). Natural gas-derived hydrogen is usually produced in large manufacturing facilities, where it is compressed and shipped to wherever it is to be used. Although this method of distribution could be suitable for such large-scale applications as electrical power plants, researchers worry

that relying on such a high-volume, high-cost method of supplying hydrogen would cripple widespread adoption of fuel cell-powered technologies. That's why finding alternative methods of producing hydrogen is so important, Kammen says.

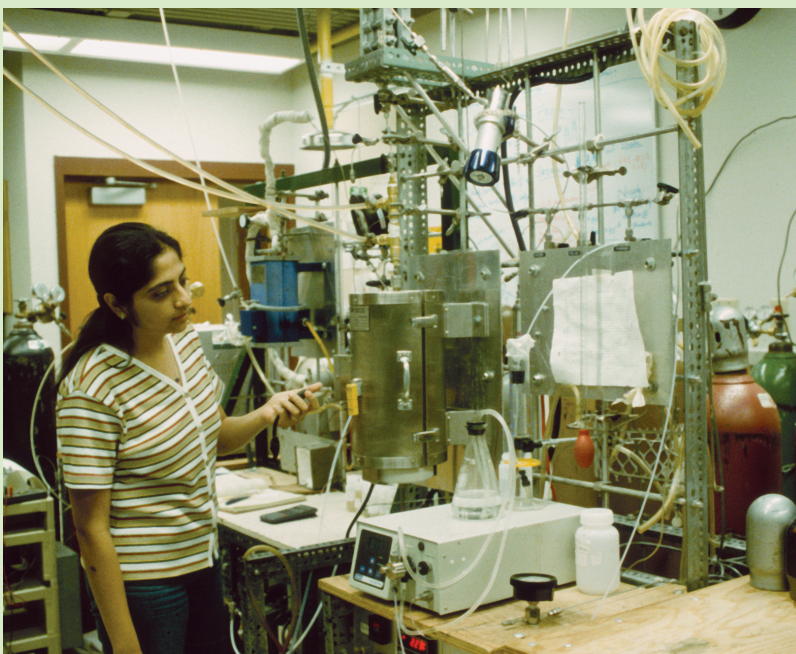
Low Temps, High Returns

Randy Cortright, a chemical engineering research scientist at the University of Wisconsin-Madison, graduate student

under moderate pressure (by comparison, the steam process runs at 430°C [806°F]). They achieve this by using a purely chemical reaction that doesn't require adding additional energy as heat. As a result, the fuels remain liquid rather than gasifying into steam, and working with the source fuel in a liquid state saves a substantial amount of energy compared to other vapor-phase processes used for biomass or conventional fossil fuels.

Another advantage of working at relatively low temperatures is that it reduces the amount of carbon monoxide (CO) in the hydrogen fuel. That's important for low-temperature fuel cells, because CO can damage their electrodes. And because it takes place at low temperatures, there is no formation of other gases, such as nitrogen oxide, which contributes to acid rain in addition to being a greenhouse gas.

Although the Wisconsin process does release CO₂, much like steam reforming of natural gas, there's a difference. The CO₂ released in the Wisconsin process was recently removed from the atmosphere by the very plants from which the



Gas pump of the future? Sustainability is the name of the game when it comes to hydrogen fuel production. The Wisconsin method (above) uses a chemical reaction at low temperatures to break down biomass, producing pure hydrogen.

Rupali Davda, and chemical engineering professor James Dumesic have developed a new way to liberate the hydrogen in renewable substances, such as plants and fats left over from processing animal products. The Wisconsin process, described in the 29 August 2002 issue of *Nature*, uses relatively pure refined energy feeds such as glycerol and glucose from corn syrup. Energy feeds can also be produced from sugar beets or in less pure forms from such organic waste sources as wood pulp and cheese whey.

The system works by breaking apart and rearranging carbon-carbon and carbon-oxygen bonds as the sugar molecules react with water on the surface of a platinum catalyst. These rearranged molecules react with the water in the sugary liquid to produce hydrogen. This process has a patent pending, and Cortright and Dumesic have a startup company to develop it called Virent Energy Systems.

One of the things that distinguishes this method from others that break down biomass is that it operates at lower temperatures of about 227°C (437°F) and

glucose feed stocks are made. On a net scale, says Cortright, the process does not generating any extra CO₂.

The Wisconsin process also has fewer stages than many other biomass hydrogen extraction methods, making it more efficient to build and operate the necessary equipment. Cortright imagines the process could someday provide on-demand hydrogen, perhaps for very small devices such as mobile phones and laptop computers as well as larger applications such as vehicles. "You would have an on-board reformer that would extract the hydrogen from that fuel and send it to the fuel cell, right on the vehicle," he says. "You can visualize filling up your car with sugar water."

But that day is years of research and engineering away, Cortright warns. This process is still at the proof-of-concept stage and has been tested only as a small, bench-top prototype. The scientists are testing different types of feed stocks, looking for catalysts that are cheaper than platinum, and in general trying to improve the system's efficiency.

Algae: Putting a Pest to Work

Another promising approach, according to Helena Chum, director of the DOE National Renewable Energy Laboratory's Division of Chemistry for Bioenergy Systems in Golden, Colorado, is using algae to generate hydrogen. For more than 60 years scientists have known that some types of algae can produce minute amounts of hydrogen. In the January 2000 issue of *Plant Physiology* scientists at the University of California at Berkeley and the National Renewable Energy Laboratory announced that they had found that the absence of sulfur nutrients triggers a "molecular switch" that forces *Chlamydomonas reinhardtii*, a type of green algae, to significantly increase the amount of hydrogen it produces. This process also has a patent pending and an associated startup company, Melis Energy.

"With this method we're talking essentially about the conversion of sunlight energy into hydrogen energy," says Anastasios Melis, a professor of enzymology at Berkeley and principal investigator for the *Plant Physiology* paper. "The strain that we use you will find anywhere out in nature. In every little puddle of water or lake, it is there."

The trick, Melis says, is to first allow the algae to grow normally, collecting sunlight and accumulating carbohydrates and other cellular fuel. Then, to trigger the switch, the algae are transferred to a sealed sulfur-free environment. Without sulfur, photosynthesis in the algae stops, which prevents the cells from producing oxygen. That in turn prevents the cells from burning internal sugars in their usual manner, through metabolic respiration. Instead, the cells activate an alternative type of metabolism, which generates hydrogen. The hydrogen rises to the top of the sealed environment and is then drawn off. If left in this state forever, the algae would die.

So periodically (after about four days of hydrogen production, says Melis) the algae must be returned to an environment that includes sulfur, and their normal photosynthesis switched back on.

An advantage of this process, Melis says, is that it produces no polluting by-products. And like the Wisconsin process, its simplicity would make it attractive for such applications as bringing electricity to developing world settings. "The application of the method is decidedly low-tech," Melis says. "There is nothing fancy about throwing a cylindrical tube on the ground, filling it up with water and some fertilizer, and growing the green algae in this controlled space."

But this process is also in its infancy, he says, and it must be made more efficient. Currently the algae produce only 15–20% as much hydrogen as theoretically possible. Scientists also need to improve different algae's thermal tolerance, because they want to expose them to as much sunlight as possible, and to temperatures higher than the plants' typically shady natural environment. "It would be desirable to try to isolate strains that are more thermal-tolerant than the ones we have in the laboratory," Melis says. Chum adds that algal hydrogen photoproduction is sensitive to the presence of oxygen, and this sensitivity is a major factor currently limiting the use of algae. New scientific approaches are being developed to overcome this limitation and increase hydrogen production.

Other Promising Techniques

Of the current biomass-to-hydrogen technologies, perhaps the closest to practical adoption, says Chum, is multistage catalytic steam reforming of pyrolysis products. Pyrolysis is a thermal process that decomposes organic materials in an inert atmosphere. It can be done under pressure

and at relatively high temperatures, above 430°C (806°F). Pyrolysis breaks molecules at their weakest points, producing a hydrogen-rich bio-oil, with carbon (which can be used as fertilizer) as a by-product. The bio-oil is then steam reformed, much as a fossil fuel would be, to liberate the hydrogen.

Because natural gas contains significantly more hydrogen than biomass by weight, it's economically prudent for the process to be part of a system that uses biomass by-products or that makes additional products, such as fertilizer, says Chum. She also says that prototypes of catalytic steam reforming systems that are fueled with peanut shells are now undergoing field tests.

Also close to commercialization are gasification processes in which biomass or its residues (for example, bagasse and peanut shells) or fast-growing plants such as switchgrass and poplar trees are heated in the presence of oxygen. Biomass gasification breaks down the polymers of biomass into a mixture of hydrogen, CO, CO₂, and other small compounds. The CO can be shifted to hydrogen gas (H₂) and CO₂ with water (either chemically at high temperature or photobiologically at room temperature), and hydrogen is the main product. Chum adds that the gas industry is actively pursuing the development of small-scale steam reforming of natural gas for use in refueling stations as well.

Any of these processes may pan out in the end, says Chum. What is just as likely to happen, she says, is that a number of different hydrogen production technologies will be developed to fill different market niches. A system in which algae gather sunlight would make more sense in sub-Saharan Africa than in South Dakota, while a system optimized to feed on corn and cheese whey would work better in the American Midwest than in China. Simple, easy-to-maintain systems, even if relatively inefficient, might work their way to developing world settings, while more complex, more efficient machines might dominate industrialized nations. And although hydrogen production using renewably generated electricity is the long-term goal, fossil fuels will likely be used during the transition, says Kammen.

"There are different conditions under which those different processes are going to be very useful," Kammen says. "The key aspect isn't which one wins, so much. It's that there is a diversity of them. Because based on local climate, the amount of water, the availability of land, et cetera, there's likely to be needs for all of these."

Scott Fields

Suggested Reading

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